CHEMICAL HAZARD SUMMARY

Canadian Centre for Occupational Health and Safety
250 Main Street East
Hamilton Ontario Canada L8N 1H6

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METHANOL

Other Names	Methyl alcohol, methyl hydrate, carbinol, wood alcohol, wood spirit. CAS 67-56-1
Description	Clear, colourless liquid with a slight alcoholic odour.

HAZARD SUMMARY

Exposure	Vapour: Inhalation Liquid: Eye contact, skin contact and ingestion
Effects of Short-Term Exposure	Vapour may cause irritation of nose, throat and eyes, headaches, vomiting, nausea, dizziness, drunkenness, blurred vision. Blindness, unconsciousness and death follow massive exposures. Poisoning can occur through skin absorption. Ingestion can cause blindness and death.
Effects of Long-Term Exposure	Headaches, giddiness, eye irritation, insomnia, abdominal pains, skin irritation, impaired vision and blindness.
Fire and Explosion Hazards	Highly flammable – burns with a very pale blue flame that is not usually visible in normal light. Dangerous fire risk. At room temperature, vapours can readily form flammable or explosive mixtures with air. Vapours may spread from the spill site and ignite. Containers may explode in heat of fire.
Fire Extinguishers	Dry chemical, alcohol foam, carbon dioxide, water spray or fog. Direct water stream should not be used since the stream will scatter and spread the fire. Use water spray to cool containers.
Chemical Reactivity	Normally stable. Contact with oxidizing agents increases risk of fire and explosion.

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Personal Protection	Wear protective clothing to prevent exposure of skin to liquid or concentrated vapours. Wear splash-proof chemical safety goggles or a face shield (8-inch minimum) for eye or face protection. Wear respirators whenever vapour concentrations exceed permissible limits. The type of respirator used will depend on the concentration of methanol in the workplace air.
Storage	Store methanol in tightly closed containers in a cool area with adequate ventilation, away from normal work areas and away from sources of heat, sparks and oxidizing agents.
Exposure Limits	As recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) 1986-87. Threshold Limit Value – Time-Weighted Average Exposure (TLV-TWA): 200 ppm (parts per million) or 260 mg/m^3 (milligrams per cubic metre) Threshold Limit Value – Short-Term Exposure Limit (TLV-STEL): 250 ppm or 310 mg/m^3 Skin — Absorption via unbroken skin, eyes, or mucous membranes may contribute to the overall exposure.

TWA is defined as the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek.

STEL is defined as a 15-minute time-weighted average exposure which should not be exceeded at any time during a workday. Exposures at the STEL should not be longer than 15 minutes and should not be repeated more than four times per day. There should be at least 60 minutes between successive exposures at the STEL.

SCOPE OF THE DOCUMENT

This summary was prepared at the Canadian Centre for Occupational Health and Safety (CCOHS) and is intended primarily as a source of information for persons who work with or may be occupationally exposed to this material. The information selected for inclusion is believed to be reliable and generally relevant to occupational health. Other information may be available which bears on particular work situations. The scientific data in many areas are limited and may allow a variety of interpretations. Additional information, corrections, comments, and questions are welcome, and should be addressed to the Inquiries Service, CCOHS, 250 Main Street East, Hamilton, Ontario, L8N 1H6, (416) 572-2981 or toll free, 1-800-263-8276.

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I. USES AND OCCURRENCE

Methanol is widely used as a solvent for lacquers, paints, varnishes, cements, inks, dyes, plastics and various industrial coatings and in the manufacture of antibiotics, hormones, steroids, vitamins and drugs.

Large quantities are used in the production of formaldehyde and other chemical products. Methanol is also used as a gasoline additive; as an ingredient in lacquer thinners, paint and varnish removers, dewaxing preparations, embalming fluids, antifreeze mixtures and duplicating fluids; as a cleaning agent for leather goods, glass and photographic film; as a poison added to alcohol to make it unfit for drinking; a flushing fluid for hydraulic systems; as an extractant in refining gasoline and removing impurities from animal and vegetable oils; in dehydrating pipelines; and as a fuel for automobiles, aircraft, picnic stoves and soldering torches.

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II. TOXICOLOGY

Routes of Exposure

Inhalation is the most likely route of exposure in the workplace. In enclosed spaces with poor ventilation, methanol vapour may reach concentrations sufficient to cause toxic effects.

Poisonings have resulted from absorption of methanol through the skin[1,2,3].

Liquid methanol may be swallowed accidentally. Methanol resembles common alcohol (ethanol) in taste and smell and has been substituted for the latter in illegal alcoholic beverages. Many instances of mass poisoning from methanol in illegal alcoholic beverages have been recorded[4,5]. In 1951, one incident resulted in 41 deaths with over 300 people poisoned[6]. As little as 4 mL (one-third to one-half ounce) may cause blindness and from 80-150 mL (three to eight ounces) have been fatal[7,8].

General information on routes of exposure is available in the CCOHS publication "How Workplace Chemicals Enter the Body"[9].

Removal from the Body

Most of the methanol taken into the body is broken down in the liver[4,8]. Formaldehyde and formic acid are produced from this breakdown and are excreted in the urine. Complete breakdown and excretion takes several days. The breakdown products are responsible for many of the toxic effects of methanol.

Effects of Short-Term Exposures in Humans

Inhalation

Short-term exposure to methanol vapour can produce irritation of the eyes, nose and throat, headache, nausea, vomiting, dizziness, lightheadednesss, giddiness, drunkenness, difficulty in breathing, dilated pupils and blurred vision[3]. Symptoms depend on the level and duration of exposure and vary considerably from person to person[1].

Industrial exposures to methanol vapours can cause death or blindness[1,2,3]. Reported incidents have often involved work in confined spaces (e.g. varnishing the inside of beer vats) at extremely high-vapour concentrations (4,000 to 12,000 ppm) for up to 12 hours[1]. Increased awareness of the dangers of methanol and improved work practices have reduced the number of serious poisonings in recent years.

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Effects on the Skin
Methanol is a mild skin irritant[3,10]. Skin may become dry and cracked because methanol removes natural oils from the skin.

Methanol can be absorbed through the skin in toxic or lethal amounts. For example, in one non-occupational incident, 21 children ranging in age from 1.5 months to 4 years were poisoned as a result of having methanol rubbed on their stomachs to relieve abdominal pains. Twelve of the 21 children died of cardiac or respiratory failure two to ten days after hospital admission[11].

Effects on the Eyes
Methanol vapours can irritate the eyes. Eye damage from contact with liquid methanol is slight and with proper treatment eyes heal within a few days[3,7].

Ingestion
Ingestion of methanol has produced blindness. Effects on vision range from spots before the eyes, blurred or double vision, changes in colour perception, pain or tenderness about the eyes, dilated pupils, avoidance or intolerance of light and partial loss of vision[7,12,13]. These early symptoms may disappear but later there may be permanent loss of vision.

In addition to effects on vision, ingestion of methanol produces weakness, nausea, vomiting, headaches, dizziness, lightheadedness and euphoria. These symptoms ressemble those of ethanol ("alcohol") intoxication. After the initial symptoms disappear a delay of 6 to 30 hours usually follows before the same symptoms reoccur, only this time in much greater severity. Victims complain of excruciating upper abdominal pain, intense vomiting, numbness and shooting pains in the arms and legs, difficulty in breathing, shortness of breath, chills, cold, clammy extremities and marked restlessness. Victims may become delirious. The most severely poisoned lose consciousness and die of respiratory or heart failure. The coma may last as long as four to six days. Those who recover from coma may be blind.

Effects of Long-Term Exposures

Long-term exposures to methanol have been associated with headaches, giddiness, eye irritation (conjunctivitis), insomnia, gastrointestinal disturbances, skin irritation, impaired vision and blindness[2]. Some of these effects may be due to repeated short-term exposures.

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Exposure to 22 to 25 ppm of methanol for nine months to two years showed no harmful effects[3].

A case of impaired vision has been reported in a worker exposed to methanol concentrations of 1,200 to 8,000 ppm for four years[14].

Reproductive Hazards
Studies in laboratory animals are widely used to indicate the potential of a chemical to cause reproductive effects in humans.

Rats breathing methanol vapours of 5,000 and 10,000 ppm for days 1 to 19, and 20,000 ppm for days 7 to 15, 7 hours/day, of pregnancy showed fetal damage only at the highest dose level[15]. This dose was toxic to the mother.

No reports were located on the effects of methanol on pregnant women.

Carcinogenic Effects
The carcinogenic activity of methanol in animals or humans has not been studied[1].

Mutagenic Effects
Methanol is not mutagenic when tested in bacterial systems such as the Ames test[3]. However, there is some evidence that a breakdown product of methanol (formaldehyde) in the body may be mutagenic. The significance of this for humans is unknown. Small amounts of formaldehyde are produced naturally in normal body processes.

Toxicity Data in Animals
The relative poisoning potential of a compound can be assessed from the LD_{50} or LC_{50} obtained in animal tests. The LD_{50} is the amount of a chemical (weight of chemical/weight of animal) which is needed to kill one-half (50%) of the test animals. The LC_{50} is the concentration in air which kills half of the animals following an exposure lasting 4 hours or other indicated time period. Test animals are usually rats, mice, or other rodents. Routes of exposure are usually oral (by mouth), dermal (absorption through the skin), or inhalation (breathing of vapour). The values for this material are:

LD_{50} (rat, oral)	6.2-13.0 g/kg[3]
LD_{50} (rabbit, dermal)	20.0 mL/kg[3]
LC_{50} (rat, 4 hours)	64,000 ppm[16]

On a scale of 1 to 6 (1 = practically non-toxic, 6 = supertoxic), methanol rates as a 3 (moderately toxic)[12].

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General information on the LD_{50} is available in the CCOHS publication "What is an LD_{50}?"[17].

III. FIRE AND EXPLOSION HAZARDS

Methanol is a flammable liquid and can pose a dangerous fire risk. It burns with a pale blue flame that is not usually visible in normal light. At room temperatures, vapours from open containers can quickly form flammable or explosive mixtures with air. The vapour is heavier than air and may travel along the ground for considerable distances to a source of ignition and flashback. Containers may explode in the heat of a fire.

Flash Point

The flash point of methanol is about 12°C (54°F). When the liquid is heated above this temperature, enough vapour is produced to form a flammable or explosive mixture of vapour and air.

Explosive Limits in Air

The lowest concentration of vapour in air which can burn or explode is called the lower flammable limit (LFL) or lower explosive limit (LEL) and is about 6.7% (67,000 ppm) for methanol. Similarly, the highest concentration of vapour in air which can burn or explode is called the upper flammable limit (UFL) or upper explosive limit (UEL) and is about 36.5% (365,000 ppm) for methanol. Between the LEL and the UEL possible hazards include explosion in confined spaces or a fire travelling along the line of vapour from a spark or flame to a container or spill (flashback).

Adequate ventilation can prevent the accumulation of explosive concentrations of vapour in work or storage areas.

Fire Extinguishing Agents

For fires involving methanol, recommended types of extinguishing agents are dry chemical, alcohol foam, carbon dioxide or water spray. Direct water stream should not be used for fighting fires involving methanol since it can cause the fire to spread. A water spray can be used to reduce the rate of burning and to cool containers.

Chemical Reactivity

Methanol is normally stable. Contact with strong oxidizing agents may increase the risk of fire and explosion.

Several reference texts provide more complete lists of chemicals which may react with methanol to form explosive reactions[10,18].

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IV. EXPOSURE CONTROL

In many operations where methanol is used in small amounts at room temperature, general or dilution ventilation may be adequate to keep exposures under control. Where mists or high vapour concentrations may be present, explosion-proof local exhaust ventilation systems should be used. Quarterly checks should be made to ensure that the ventilation system is functioning properly.

In some situations, such as working in enclosed spaces and in some maintenance operations, personal and respiratory protective equipment are essential when effective ventilation and engineering controls are not possible.

Protective Clothing
Wear protective clothing (gloves, aprons, coveralls, boots) as needed to prevent exposure of skin to liquid or concentrated vapours. Methanol is a strong solvent and many materials do not provide adequate protection. Clothing made with butyl rubber, nitrile rubber and Viton can resist penetration and degradation by methanol[10,19]. Clothing coated with chlorinated polyethylene, natural rubber, neoprene or polyurethane can also provide good protection. Polyvinyl alcohol and polyvinyl chloride appear to be unsuitable for protection against penetration by methanol.

Any clothing which becomes contaminated with methanol should be removed promptly and discarded or laundered separately and thoroughly dried before re-use.

Wear splash-proof chemical safety goggles or a face shield (eight-inch minimum) whenever there is a risk of splashing liquid into the eyes.

Eye-wash fountains and safety showers should be located in areas where methanol splashes are likely to occur.

Respiratory Protection
Factors to be considered when implementing a respiratory protection program include:

Selection of appropriate respirators	Inspection
Respirator fit testing	Cleaning
Respirator maintenance	Program evaluation
	Worker training

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These factors are described in more detail in CSA Standard Z94.4 "Selection, Care, and Use of Respirators", available from the Canadian Standards Association.

The degree of respiratory protection required depends on the concentration of the vapour and the duration of the exposure. Because of the poor warning properties of methanol, use of air-purifying respirators is not advisable. NIOSH[20] recommends the following respiratory protection for methanol vapour concentrations*:

Vapour concentration of 2,000 ppm (2,600 mg/m^3) or less:
Any supplied-air respirator, or
Any self-contained breathing apparatus.

Vapour concentration of 5,000 ppm (6,550 mg/m^3) or less:
Any supplied-air respirator operated in a continuous flow mode.

Vapour concentration of 10,000 ppm (13,000 mg/m^3) or less:
Any self-contained breathing apparatus with a full facepiece, or
Any supplied-air respirator with a full facepiece, or
Any supplied-air respirator with a tight-fitting facepiece operated in a continuous flow mode.

Vapour concentration of 25,000 ppm (32,750 mg/m^3) or less:
Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive-pressure mode.

Emergency or planned entry in unknown concentration or IDLH conditions**:
Any self-contained breathing apparatus with full facepiece and operated in a pressure-demand or other positive-pressure mode, or
Any supplied-air respirator with a full facepiece and operated in pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

Escape:
An appropriate escape-type self-contained breathing apparatus.

*Note: The above recommendations apply only to equipment approved by NIOSH or MSHA.

**Note: For the purpose of respirator selection, the Immediately Dangerous to Life or Health (IDLH) level represents the maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.

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V. SMALL-SCALE STORAGE AND HANDLING

Store methanol in tightly-closed, electrically-grounded containers in a cool area separate from normal work areas. Provide adequate ventilation to the storage area. Ensure there are no sources of heat, flames or sparks. Approved safety solvent containers are required. Cover containers when not in use and store in a fire-resistant grounded cabinet. Use spark-resistant electric switches and motors (fans, refrigerators). Prohibit smoking in or near a storage area.

Use methanol in minimal quantities in designated areas with adequate ventilation and away from sources of heat or sparks and oxidizing agents. Ground containers during mixing or transfer. Whenever possible, use fire-resistant containers. Wear appropriate protective equipment to prevent skin and eye contact.

Clean-Up and Disposal
Provide adequate ventilation, protective clothing and appropriate respirators. Remove all sources of heat, sparks or flame before attempting to clean a spill. Stop the flow if it can be done safely. Contain spilled material. For small quantities, absorb spills on paper towels and allow vapours to evaporate in a safe place (such as a fume hood). Larger quantities may be collected in sand, dry clay or other absorbent materials and placed in sealable containers for later disposal.

Consult the federal, provincial and local governments for advice on disposal. Waste methanol must never be discharged directly into sewers or surface waters. Large quantities of waste methanol can be disposed of at designated landfill sites or incinerated at approved sites. It can also be reclaimed by filtration and distillation.

VI. FIRST AID

The following general procedures are suggested for first aid involving poisoning by methanol:

Inhalation
Remove the source of contamination if this can be done safely or move the victim to fresh air. If breathing has stopped, properly trained personnel should begin artificial respiration or cardiopulmonary resuscitation (CPR) immediately. Obtain medical attention immediately.

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Skin
As quickly as possible, flush the contaminated area with lukewarm, gently running water for at least 20 minutes. Remove contaminated clothing promptly and discard or launder separately. Dry thoroughly before re-use.

Eyes
As quickly as possible, flush the contaminated eye(s) with lukewarm, gently flowing water for 20 minutes, holding the eyelid(s) open. Obtain medical attention immediately.

Ingestion
When methanol has been swallowed, obtain medical attention immediately. Never give anything by mouth if the victim is rapidly losing consciousness or is unconscious or convulsing. DO NOT INDUCE VOMITING. Victim may drink 8 to 10 ounces (240 to 300 mL) of water to dilute material in the stomach. If vomiting occurs naturally, the victim should lean forward to reduce the risk of drawing liquid methanol into the lungs.

Note: Consult a physician and/or the nearest Poison Control Centre for all cases of ingestion or eye contact and all but trivial cases of inhalation or skin contact.

VII. EXPOSURE LIMITS

In many Canadian jurisdictions, exposure limits are similar to the Threshold Limit Values (TLVs) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). For methanol the 1986-87 recommended TLVs are:

1. Threshold Limit Value-Time Weighted Ave age (TLV-TWA) =
   200 parts per million (ppm) or 260 milligrams per cubic metre (mg/m^3):

   This is "—the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect."

2. Threshold Limit Value-Short Term Exposure Limit (TLV-STEL) =
   250 parts per million (ppm) or 310 milligrams per cubic metre (mg/m^3):

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"A STEL is defined as a 15-minute time-weighted average exposure which should not be exceeded at any time during a workday even if the eight-hour time-weighted average is within the TLV. Exposures at the STEL should not be longer than 15 minutes and should not be repeated more than four times per day. There should be at least 60 minutes between successive exposures at the STEL."

"The STEL is not a separate independent exposure limit, rather it supplements the time-weighted average (TWA) limit where there are recognized acute effects from a substance whose toxic effects are primarily of a chronic nature. STELs are recommended only where toxic effects have been reported from high short-term exposures in either humans or animals."

3. Skin

Absorption via the unbroken skin, eyes, or mucous membranes may contribute to the overall exposure. This applies to direct contact with the substance or to contact with airborne material. Other substances in which the material is dissolved or with which it is mixed can alter skin absorption.

Certain Canadian jurisdictions have adopted the entire set of ACGIH TLVs for chemical substances by reference in their regulations. Others use the TLVs as guidelines for control of airborne contaminants. Still others specify exposure limits for chemical substances, including methanol, in their regulations. Since the manner in which exposure limits are established, interpreted and implemented can vary among the jurisdictions, detailed information should be sought from the appropriate government agency in each jurisdiction.

According to the preface in the ACGIH booklet:

"Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. Because of wide variation in individual susceptibility, however, a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness."

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"Threshold limits are based on the best available information from industrial experience, from experimental human and animal studies and, when possible, from a combination of the three."

"The TLV-TWA should be used as guides in the control of health hazards and should not be used as fine lines between safe and dangerous concentrations." (Reproduced by permission of the ACGIH).

Warning Properties of Methanol at the Exposure Limit
The odour or irritating effects of methanol vapour do not provide adequate warning of the presence of hazardous concentrations of methanol. The odour threshold of methanol ranges from 1,500 to 5,900 ppm[1].

Exposure Limits in Other Nations
The approaches or mechanisms for establishing and applying occupational exposure limits can vary widely from country to country. Information on exposure limits in a number of foreign jurisdictions is available from CCOHS.

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VIII. CHEMICAL AND PHYSICAL PROPERTIES

CAS registry number	67-56-1
Chemical formula	CH_4O
Chemical structure	CH_3OH

Physical Properties

Boiling point	64.7°C (148.1°F)
Melting point	-97.7°C (-144°F)
Density	0.7915 (water = 1)
Solubility	miscible (soluble in all proportions) in water
Vapour pressure	160 mm Hg (at 30°C)
Vapour density	1.11 (air = 1)
Odour threshold	1,500 to 5,900 ppm
Flash point	12°C (54°F) (closed cup)
Autoignition temperature	385°C (725°F)
Explosive limits	upper 36.5% lower 6.7%

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Note: Additional references on this subject are available from CCOHS upon request.

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